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“Doping Group IIB metal ions into quantum dot shells via the one-pot decomposition of metal-dithiocarbamates”

Joseph C. Bear, Nathan Hollingsworth, Anna Roffey, Paul D. McNaughter, Andrew G. Mayes, Thomas J. Macdonald, Thomas Nann, Wing H. Ng, Anthony J. Kenyon, Graeme Hogarth and Ivan P. Parkin**

Dr. Joseph C. Bear, Dr. Nathan Hollingsworth, Dr. Anna Roffey, Dr. Graeme Hogarth, Prof. Ivan P. Parkin
Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK. Email: i.p.parkin@ucl.ac.uk

Dr. Paul D. McNaughter, Dr. Andrew G. Mayes
School of Chemistry, University of East Anglia, Norwich Research Park, Norwich, Norfolk NR4 7TJ, UK.

Thomas J. Macdonald, Prof. Thomas Nann
Ian Wark Research Institute, University of South Australia, Mawson Lakes Boulevard, Adelaide, SA 5095, Australia.

Dr. Wing Ng, Prof. Anthony J. Kenyon
Department of Electronic and Electrical Engineering, University College London, Torrington Place, London, WC1E 7JE, UK.

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Abstract: ((An investigation into the doping of group IIB metal ions into the shells of II-VI and III-V semi-conductor core/shell quantum dots is presented. The effect of Cu doping developed in our previous study on CdSe/ZnS-CuS particles is also examined. The shells consist of ZnS and doped metal sulphide, obtained from the decomposition of metal dithiocarbamates; single-source precursors. The photoluminescence properties of the quantum dots changed profoundly, with infrared emission achieved using Hg as a shell dopant. Quantum dots were characterised and interrogated using TEM, HRTEM, electron diffraction, ToF-SIMS, XPS, EDS spectroscopy, photoluminescence emission and lifetime spectroscopy and UV/vis spectroscopy.

1. Introduction

((Over the past two decades, intense research has gone into the improvement of quantum dot properties and the diversification of their use.^[1–5] The vast majority of research has been directed into improving the optical properties of quantum dots by increasing quantum yields (QYs),^[6–8] photostability,^[9,10] increasing the range of optical activity^[11–13] and eliminating “blinking”.^[14–16]

Enhancement of the optical properties and QYs relies on the reduction of surface defects in the QD lattice fringes. These surface defects “trap” excitons, preventing electron-hole recombination. This leads to a broadening of the QD photoluminescence and a reduction in QY.^[17–20]

In 1990, Kortan *et al.*^[21] reported that an overgrowth of a shell with a larger band gap than the QD core dramatically improves the photoluminescence and QY, due to better quantum confinement of the exciton in the QD core by a semi-conducting material. Lattice matching between the core and shelling materials is paramount, as this reduces the amount of surface defects and leads to a higher overall QY. A QD shell also prevents QD core photo-oxidation which results in a periodic decline in photoluminescence.

Organometallic routes towards the overgrowth of a shell have led to vastly improved quantum yields and pushed QD materials and devices towards commercial viability.^[22–24] Bawendi and co-workers developed the first organometallic route to a zinc sulphide (ZnS) shell around CdSe QDs,^[25] whereby a slow injection of diethylzinc and 1,1,1,3,3,3-hexamethyldisilathiane as the sulphur source were utilised, both pyrophoric and toxic materials. Since then, the use of fatty acid salts of zinc and elemental sulphur have been reported, but these routes require multiple injection steps.^[26,27]

A more attractive approach is the use of air-stable, single-source precursors, which decompose at low temperatures, yielding the desired material. Metal dithiocarbamates represent a class of compounds which decompose to yield corresponding metal sulphides.

This approach has been used successfully by our group to yield highly crystalline metal-sulphide nanoparticles in oleylamine.^[28] It has been shown that zinc diethyldithiocarbamate can be used to grow a ZnS shell of tunable size around QDs in the presence of surfactants.^[24,29,30] However, the use of different metal-dithiocarbamates for shell synthesis and for the furtherance of QD optical properties has been under-explored.

In this study, we present the synthesis of QD shells containing a mixture of zinc sulphide with metal dopants (Cd, Hg and Cu) in differing ratios and an investigate their photoluminescence properties. The doping of copper metal ions into CdSe/ZnS detailed in our previous study^[30] is also placed under more rigorous scrutiny.

Synthesis and characterisation of QDs

CdSe (*n*-type, II-VI) (**a**) and InP (*p*-type, III-V) (**b**) QDs were synthesised using a hot-injection method described elsewhere.^[31–33] The QDs were then shelled by decomposing a mixture of zinc(II) diethyldithiocarbamate and metal dithiocarbamate [M = Cd (**1a**, **1b**), Hg (**2a**, **2b**), Cu(**3a**)] complexes at 120 °C for 2 hours in the presence of 1-octadecene, trioctylphosphine and oleylamine. The molar ratios of Zn to metal dithiocarbamates (**1-3**) used were: 1-1, 3-1, 7-1 and 15-1 unless stated otherwise.

ZnS was chosen as a shell “matrix” in order to preserve luminescence and colloidal stability due to the ability of ZnS to provide good lattice matching between the QD core and shell on numerous semi-conducting nanocrystals.^[24,34–36]

As-synthesised QDs were analysed using transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM), with all yielding monodisperse nanocrystals between 3 and 5 nm in diameter (**Figure 1**).

Other characterisation techniques including: X-Ray photoelectron spectroscopy (XPS), Energy dispersive X-Ray spectroscopy (EDS), Time-of-flight secondary ion mass spectroscopy (ToF-SIMS), photoluminescence spectroscopy, UV-visible spectroscopy and photoluminescence lifetime spectroscopy were used.

[Figure 1]

Cd doping (1a, 1b)

Cd doping afforded a visible increase in brightness of the resultant CdSe/ZnS-CdS QDs and an increase in the average size of the quantum dots ranging from 3.43 nm for the lowest Cd dopant level to 4.50 nm- a size increase mirrored by the increasing band-gap in the photoluminescence spectra (*vide infra*). EDS and XPS both showed the ratio of Cd to Se in the unshelled CdSe cores to be the expected 1:1. Surprisingly, upon the overgrowth of a pure ZnS shell both XPS and EDS showed this ratio changed to 2:1 indicating reduced levels of Se (see table S2.1 and 3.1). Doping the ZnS shell with Cd resulted in the same 2:1 ratio of Cd to Se for the lower dopant levels (15:1). As expected, EDS and XPS results show an increase in Cd at. % through the sample with increased levels of doping (see table S2.1 and 3.1). Cd doping in InP/ZnS-CdS at the 15:1 Zn to Cd indicates a 4.28 at. % of cadmium and a decrease in the ratio of In versus P when compared to the pure InP cores, suggesting In replacement by Cd in the InP lattice.

Due to a combination of the excitation area of the EDS and the depth etch of XPS both being larger than the QDs, information with regard the location of the dopant is difficult to ascertain. In order to determine information of this nature the materials were scaled up, thereby allowing depth analysis. Trends seen on these bulk samples can then tentatively be

suggested to be apply in the QD on the nanoscale. To do this 1:1 molar ratio of zinc(II) diethyldithiocarbamate to cadmium(II) diisobutyldithiocarbamate was deposited on bulk CdSe powder using the same shelling protocol applied in **1a**.

ToF-SIMS data taken on this sample showed a marked decrease in Zn concentration as the sample is etched, and a very gradual decrease in Cd concentration. This would indicate in using our shelling protocol zinc would act as a shelling medium and Cd would be present in both the shell and core (see figure S1.1) indicating that Cd can act as a dopant within the ZnS lattice. It is noteworthy that the average sizes of the QDs increased on addition of Cd to the ZnS shell and indeed other metal dopants in a linear fashion, with the highest levels of doping yielding the largest QDs (see table S7.1). The average lattice spacings indicated no discernible change in the structures of the different doping levels of CdSe/ZnS-CdS (**1a**) or InP/ZnS-CdS (**1b**), with average *d*-spacings of 0.318 nm and 0.328 nm recorded respectively by HRTEM (see table S7.1 and figure 2C).

Hg doping (2a, 2b)

On addition of CdSe QD cores to a solution of mercury(II) diethyldithiocarbamate in hexane resulted in the instantaneous formation of a black dispersion, indicating a spontaneous reaction. It is well known that mercury has a high affinity for alloying with selenium, a property that makes it a very potent neurotoxin.^[37,38] This spontaneous decomposition was not observed when shelling the InP cores. In the attempted shelling CdSe and InP with Hg doped ZnS (**2a, 2b**) HRTEM analysis revealed CdSe and InP QDs gave an average *d*-spacing of values of 0.322 and 0.314, corresponding to the <111> planes of CdSe and InP respectively, thus the overgrowth of a shell did not affect the crystalline structure of the core material (figure 1 and 2).^[11]

Quantitative EDS and XPS analysis of CdSe/ZnS-HgS QDs (**2a**) indicated an increase in the concentration of Hg with increased doping levels in a similar trend to that seen in **1a** (see tables S2.1 and S3.1). Crucially, despite the strong affinity of Hg for Se, Cd was detected by both XPS and EDS, which rules out a complete exchange of Cd atoms in the core. In addition the Cd:Se ratio remain at ca. 2:1, a similar ratio seen in XPS and EDS analysis of both pure ZnS shelled CdSe and **1a**. Again supporting the conclusion that the incorporation of Hg in the ZnS shelling matrix has little effect on the QD core composition.

[Figure 2]

XPS spectra were typical for reported core/shell QDs for CdSe/ZnS-HgS and InP/ZnS-HgS. Hg containing samples used the Hg4d area between 350 and 385 eV rather than the more conventional Hg4f or Hg5d due to masking elements, particularly Si2p masking of Hg4f, as all QD samples for analysis were mounted on glass prior to analysis (figure 3).^[39–42]

[Figure 3]

To gauge the location of the Hg within the doped samples ToF-SIMS analysis was performed on a sample of bulk CdSe coated using the shelling protocol with a 1:1 ratio of mercury(II) diethyldithiocarbamate and zinc(II) diethyldithiocarbamate. This showed an increase in the Cd concentration with increasing etch time, indicating cadmium would be present in the QD core only, in contrast to that seen in the CdS-ZnS shelling in **1a**. Zn concentration decreases with etch time indicating ZnS is acting as a shell over the CdSe. The Zn concentration trend is similar to that observed ToF-SIMS of the Cd doped sample in **1a**. Unfortunately, mercury atoms have a very low ionisation efficiency for ToF-SIMS, which

renders them practically undetectable by this method, and as such we can only postulate as to the final composition of the shell in CdSe/ZnS-HgS QDs. A core/shell/shell type system comprising CdSe/HgS-Se/ZnHgS or CdSe/HgS/ZnS seem to be the most promising candidates, the spontaneous decomposition of mercury(II) diethyldithiocarbamate within the CdSe QD cores suggests the former maybe more likely.

For InP/ZnS-HgS QDs (**2b**) however, the reaction between the InP cores and the mercury(II) diethyldithiocarbamate was not instantaneous and required heating to affect. We therefore postulate that this system behaves in a similar fashion to Cd shell doping and is therefore a InP core with doped Hg, ZnS shell.

Cu doping (3a)

Cu doping as into a ZnS shell upon a CdSe core has been previously described in our earlier work.^[30] However analysis of dopant location was not reported. Shelling a sample of bulk CdSe with a 1:1 ratio of copper(II) diethyldithiocarbamate and zinc(II) diethyldithiocarbamate and analyzing it by ToF-SIMS analysis revealed a general decrease in the amount of Cu and Zn as etch time increases with a concurrent increase in Cd, demonstrating the location of the Cu at the surface and therefore in the QD shell (figure S1.3).

Optical properties

Optical properties of the QDs altered drastically upon shelling with different ZnS/metal sulphide composite shells. The increase in QY upon shelling with ZnS has been well documented.^[7,24,29,33] In this work a similar trend was observed whereby the QY of CdSe

(29.8 %) and InP (13.6%) is increased on ZnS shelling (45.24%, 33.72% CdSe and InP respectively).

Shelling the QD cores (CdSe, InP) with a mixture of M/Zn dithiocarbamate (M= Cd, Hg) has varying effects on the overall QD photoluminescence. We have shelled CdSe and InP cores with ZnS doped with Cd, Hg and analyzed the effect of the dopands on the spectroscopic properties of the particles to ascertain trends as the group 10 triad is descended. Optical properties of previously reported Cu doped ZnS shelled CdSe QDs is scrutinized more thoroughly.

Cadmium doping (1a, 1b)

Doping of Cd in the ZnS shell of CdSe (**1a**) surpasses the QY increase afforded by pure ZnS shelling (45.24 % for ZnS, 52.04 % for CdS-ZnS). It has been shown that an “inter” shell of CdS improves the QY by smoothing out the lattice mismatch between core and shell.^[43] It was found that the higher the ratio of Cd to Zn, the more red-shifted the luminescence. This is due to the overall particle size increasing due to greater doping of heavier atoms, as the ZnS lattice has to distort to incorporate the larger Cd dopant. This allows the wavefunction of the core to reach further into the shell, hence the luminescence is red-shifted.^[44,45]

[Figure 4]

In general for Cd-doped ZnS shells, it was found that the band gap decreases with increasing amounts of Cd (see figure S5.1). Figure 1 shows absorbance and photoluminescence spectra for CdSe/ZnS QDs that have been shelled with different ratios of Zn:Cd.

The photoluminescence quantum yields (QYs) of the QDs did not follow any systematic trend: the lowest concentration of Cd caused a significant decrease of the QY to approximately 5%, while higher concentrations yielded up to 52% (ratio 7:1). Photoluminescence lifetime traces have been fitted with a stretched exponential (equation 1).

$$I = I_0 + A \exp\left(-\frac{t}{\tau}^\beta\right) \quad \text{Equation 1}$$

Where " τ " is the characteristic lifetime, " β " the stretching exponent and " A " the pre-exponential factor. This function has been chosen to reflect the fact that the luminescence lifetimes of QDs consist of a broad distribution of lifetimes, caused by a multitude of available recombination pathways. A stretching exponent of $\beta=1$ represents a single exponential decay, whereas smaller values indicate a broader distribution. Table 1 shows the luminescence lifetimes and stretching exponents of the Cd doped QDs. A slight increase of the luminescence lifetimes and a narrowing of the distribution can be observed with increasing Cd concentration. This indicates an increase in the number of defects when adding Cd to the shell synthesis.

Sample	τ (ns)	β
15:1	8.83 +- 0.04	0.668 +- 0.002
7:1	18.8 +- 0.08	0.859 +- 0.003
3:1	15.76 +- 0.05	0.828 +- 0.002
1:1	16.89 +- 0.63	0.83 +- 0.026

Table 1: Luminescence lifetime and stretching exponents of Cd doped QDs.

These results stand in stark contrast to data obtained by others for core/shell/shell type CdSe/CdS/ZnS QDs,^[43] as the number of defects decrease with the formation of a CdS intermediate shell, which leads to the conclusion that Cd atoms “dope” the ZnS shell at low concentration and form a (Cd/Zn)S alloy at higher concentrations. This finding has been supported by time-of-flight secondary ion mass spectroscopy (ToF-SIMS) on model systems, which indicates the QDs would have a high concentration of Cd on the outer surface of the particles (figure S1.1, ESI).

InP/ZnS-CdS QDs (**1b**) exhibited similar QYs than the InP/ZnS counterparts, and not the large increase shown by CdSe/ZnS-CdS (e.g., 35.0, 33.7 % for **1b** and InP/ZnS respectively), due to the increase in surface defects possibly brought about by the distortion of ZnS lattice and greater lattice mismatch affected by large Cd atoms (table S6.2). This conclusion is supported by longer photoluminescence lifetimes for InP/ZnS vs. InP/ZnS-CdS (τ values of 40 and 33 ns respectively).

Mercury doping (2a, 2b)

Introducing Hg to the ZnS shelling of CdSe QDs results in a significant red-shift of the photoluminescence, compared to CdSe/ZnS or CdSe/ZnS-CdS. Figure 5 shows the UV/vis absorption and photoluminescence spectra of QDs with different amounts of Hg added to the ZnS shell synthesis. While the 60:1 sample shows clear features of the CdSe core, the 5:1 particles luminesce at around 950 nm, which is beyond what is possible with the band-gap of CdSe. Therefore, the photoluminescence in these QDs cannot stem from the CdSe cores but possibly from the overgrowth of a luminescent HgS shell, creating an electronic sub-band from which type II system photoluminescence can occur.^[24] The overgrowth of such a shell is supported by our QD characterisation, see earlier section.

[Figure 5]

Similar to the observations made with Cd doping, the photoluminescence lifetimes increased to values about 40 ns with stretching exponents of about 0.8 when increasing the Hg concentration in the shell synthesis. This increase in photoluminescence lifetime can be attributed to an increase in the number of defects and increased lattice strain introduced through the incorporation of large, Hg atoms into the QD shell.

Doping Hg into the ZnS shell on InP QDs is not spontaneous although it can be achieved through heating. The resulting QDs show a blue-shift in luminescence, a slight increase in luminescence lifetime (from about 40 ns to 47 ns) and a similar photoluminescence quantum yield. From these results it can be concluded that ZnS-HgS shelling in InP/ZnS-HgS QDs behaves in a similar way to CdSe/ZnS-CdS QDs. When heated, the InP core starts to ‘shrink’ due to increased defect formation (causing the blue-shift in luminescence). Most likely, Hg exchanges against Zn in the shell and starts to ‘etch’ the core under these conditions.

Copper doping (3a)

Doping Cu into ZnS shells on CdSe QDs was found to reduce the overall photoluminescence of the QDs dramatically, and introduce a defect into the CdSe lattice. This causes a long-lived emission centred around 660 nm. However, previous work has shown these QDs to be an effective source of Cu^+ ions for catalysing Huisgen “click” chemistry.^[30]

Cu doping of ZnS shells for CdSe/ZnS QDs led to a sharp decrease in QY and blue shift in luminescence,^[30] a different type of behaviour to that seen for the other metal ions in this study. It was found experimentally that on increasing the copper dopant relative to zinc in

the shell increased a broad emission feature at 660 nm as well as the relatively sharp CdSe band edge emission at 550 nm. Both features were investigated with photoluminescence lifetime measurements, with the broad emission feature exhibiting a significantly longer lifetime than the CdSe band edge luminescence. Defect formation which could be due to Se/Cd vacancies on the boundary between core and shell is one possibility and is seen in CdSe QDs.^[46,47]

[Figure 6]

Low levels of Cu were detected in the QDs, and the blue shifting of the luminescence indicates a shrinking of the effective QD diameter, so it is reasonable to assume that Cu exchanges against Cd in the QD as highlighted in the literature.^[48,49] According to our previous study, Cu is released into solution upon UV irradiation, however a large amount will still remain on the surface. Indeed, Isarov and Chrysochoos investigated increasing the concentration of copper(II) perchlorate on CdS QDs in 2-propanol.^[50] They found that the photoluminescence developed a second feature and blue-shifting of the CdS band-edge photoluminescence occurred with increasing copper concentration. Isarov and Chrysochoos postulated the formation of small Cu₂S nanoparticles on the surface after ion exchange with Cd²⁺ with Cu²⁺ in solution. The poor solubility product of Cu₂S and CuS compared to that of Cd²⁺ is the driving force behind the ion exchange, with QD excitation reducing Cu²⁺ to Cu⁺. This, coupled with vigorous photo-oxidation of the QD shell, certainly supports our previous conclusions for photo-activated Cu⁺ metal release.

Tof-SIMS depth profiles of these particles confirmed the above hypothesis (figure S1.3). An increased concentration of Cu was found on the surface of the particles, however,

Cu reaches into the cores, where a decreased concentration of Cd was found compared with the CdSe/ZnS standard.

Conclusion

In conclusion, we have investigated a one-pot method of shelling CdSe and InP QDs *via* the decomposition of metal dithiocarbamates. QDs were synthesised with a standard phosphine-directed hot-injection method, and shelling mixtures were composed of differing ratios of zinc diethyldithiocarbamate and the dopant metal dithiocarbamate precursor.

Different metal dithiocarbamates were synthesised and decomposed onto the QD surface. Different metal dopants including: Zn, Cd, Hg and Cu were added, and the effects on photoluminescence studied. It was found that mercury(II) diethyldithiocarbamate decomposed instantaneously onto CdSe QD surfaces, before Zn decomposed, potentially creating a core/shell/shell type structure. Hg also red-shifted the photoluminescence significantly, primarily due to the creation of a low energy electronic sub-band, creating a type II QD system. However, further work is required to elucidate the exact composition and mechanism of photoluminescence.

Cu doping reduces the photoluminescence and quantum yield of CdSe QDs drastically. A second feature also appears in the photoluminescence spectra, most likely caused by surface defects and localised ion-exchange on the core/shell boundary.

A shell of ZnS red-shifts QD photoluminescence due to leaking of the exciton into a larger band-gap shell. The quantum yield also increases due to a reduction in surface defects and through the shielding of an easily oxidised surface. Shelling with a mixture of CdS and ZnS has a similar effect, insofar as the photoluminescence is red-shifted (but to a greater extent than just ZnS due to the larger atomic radius of Cd).

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The method we present can ostensibly be applied to any type of colloidal nanocrystal, with any combination of dopants. We have also shown that photoluminescence properties of QDs can be tuned by the amount of metal dopant in the QD shell, with infrared emission profiles easily achievable, with tremendous potential for use in solar cells.

Experimental Section

Synthesis of metal(II) diethyldithiocarbamate:

In a typical synthesis $\text{NaS}_2\text{N}(\text{CH}_2\text{CH}_3)_2 \cdot 3\text{H}_2\text{O}$ (2.65 g, 11.74 mmol) dissolved in deionised water (40ml) was added dropwise to a solution of $\text{MCl}_2 \cdot x\text{H}_2\text{O}$ ($\text{M} = \text{Zn, Cd, Hg, Cu}$, 5.87 mmol) dissolved in deionised water (40ml), forming a precipitate. The mixture was stirred for 2 hrs, filtered, washed with deionised water ($3 \times 30 \text{ mL}$) and evaporated to dryness. The product was then dissolved in dichloromethane (50 ml) and stirred with magnesium sulphate for 30 mins, after which the mixture was filtered and the filtrate dried *in vacuo*. The product was re-crystallised from chloroform.

$\text{M} = \text{Cd}$ Yield 2.03g, 85%. Anal. Calc. (found) for $\text{C}_{10}\text{H}_{20}\text{N}_2\text{S}_4\text{Cd}$: C, 29.37 (29.39); H, 4.93 (4.95); N, 6.85 (6.83).

$\text{M} = \text{Hg}$ Yield 2.75g, 94%. Anal. Calc. (found) for $\text{C}_{10}\text{H}_{20}\text{N}_2\text{S}_4\text{Hg}$: C, 24.16 (24.15); H, 4.06 (4.07); N, 5.64 (5.62).

$\text{M} = \text{Cu}$ Yield 1.84g, 87%. Anal. Calc. (found) for $\text{C}_{10}\text{H}_{20}\text{N}_2\text{S}_4\text{Cu}$: C, 33.36 (33.33); H, 5.60 (5.58); N, 7.78 (7.74)

Synthesis of CdSe QDs:

CdSe QDs were synthesised according to Roullier *et al.*^[31] with modifications. Briefly, a nitrogen-purged three necked flask was charged with cadmium(II) oxide (0.0514 g, 0.4 mmol), 1-dodecylphosphonic acid (0.220 g, 0.88 mmol), hexadecylamine (1.928 g, 8 mmol) and trioctylphosphine oxide (3.71 g, 9.6 mmol). The mixture was vacuum/back-filled with nitrogen 3 times before heating to 320 °C, for 1 hour, until the solution turned colourless. The temperature was subsequently lowered to 270 °C. 8.2 ml of a solution of selenium (0.315g, 4 mmol) in trioctylphosphine (10 ml, 22.4 mmol) was rapidly injected, and the QDs allowed to grow for two minutes before rapid cooling with boiling water. The flask was allowed to cool

to room temperature, before addition of chloroform (10 ml). CdSe QDs were precipitated with ethanol (~80 ml), isolated by centrifugation (5 minutes at $3000 \times g$). The QDs were washed twice with ethanol (2×60 ml) to remove any unbound surfactants, and dispersed in *n*-hexane (10 ml).

Synthesis of InP QDs:

Indium phosphide QDs were synthesised according to Xu *et. al.*^[32,33] Briefly, a nitrogen-purged Schlenk flask was charged with stearic acid (28.5 mg, 0.1 mmol), zinc undecylenate (86 mg, 0.2 mmol), indium(III) chloride (22 mg, 0.1 mmol) and hexadecylamine (48 g, 0.2 mmol). 1-octadecene (2 ml) was added, and the mixture vacuum/back filled with nitrogen 3 times before heating to 270 °C. On reaching 270 °C, a solution of tris(trimethylsilyl)phosphine (1 ml, 0.1 M) in 1-octadecene was rapidly injected, and the solution heated at 240 °C for 20 minutes to allow the QDs to grow. The flask was then placed in water to cool to room temperature, before addition of toluene (4 ml). InP QDs were precipitated with ethanol (~80 ml) and isolated by centrifugation (5 minutes at $3000 \times g$). The QDs were washed twice with ethanol (2×60 ml) to remove any unbound surfactants, and dispersed in *n*-hexane (10 ml).

Synthesis of ZnS-metal shells:

A shell of ZnS was synthesised by the thermal decomposition of zinc(II) diethyldithiocarbamate with cadmium(II), copper(II) or mercury(II) dithiocarbamates as dopants according to a modified procedure by Dethlefsen and Døssing.^[29] Briefly, a nitrogen-purged three-necked flask was charged with zinc(II) diethyldithiocarbamate (1.40 mmol- x mmol), dependent on ratio of Zn to metal dopant required) and a given metal dithiocarbamate (1.40 mmol – x mmol). The mixture was subjected to 3 vacuum/nitrogen flushes before injection of 1-octadecene (10 ml), trioctylphosphine (3 ml, 6.73 mmol) and oleylamine (3 ml,

9.12 mmol). The CdSe QD solution in hexane was injected, and the solution heated to 70°C at a rate of 2.2°C/min and hexane removed *in vacuo*. The solution was then heated to 120°C at a rate of 2.2°C/min and maintained at that temperature for 2 hours. The reaction was allowed to cool to room temperature before addition of ethanol (60 ml) and the CdSe/ZnS QDs isolated by centrifugation at 3000 × *g*. The QDs were washed twice with ethanol (2 × 60 ml) to remove any unbound surfactants and unreacted dithiocarbamates, and dispersed in *n*-hexane (10 ml).

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Figure 1. ((TEM micrographs and electron diffraction patterns of doped QDs. A: CdSe/ZnS-
CdS 1-1, B: InP/ZnS 15-1, C: electron diffraction pattern of A, D: electron diffraction
pattern of B, E: CdSe/ZnS QDs and F: InP/ZnS QDs.))

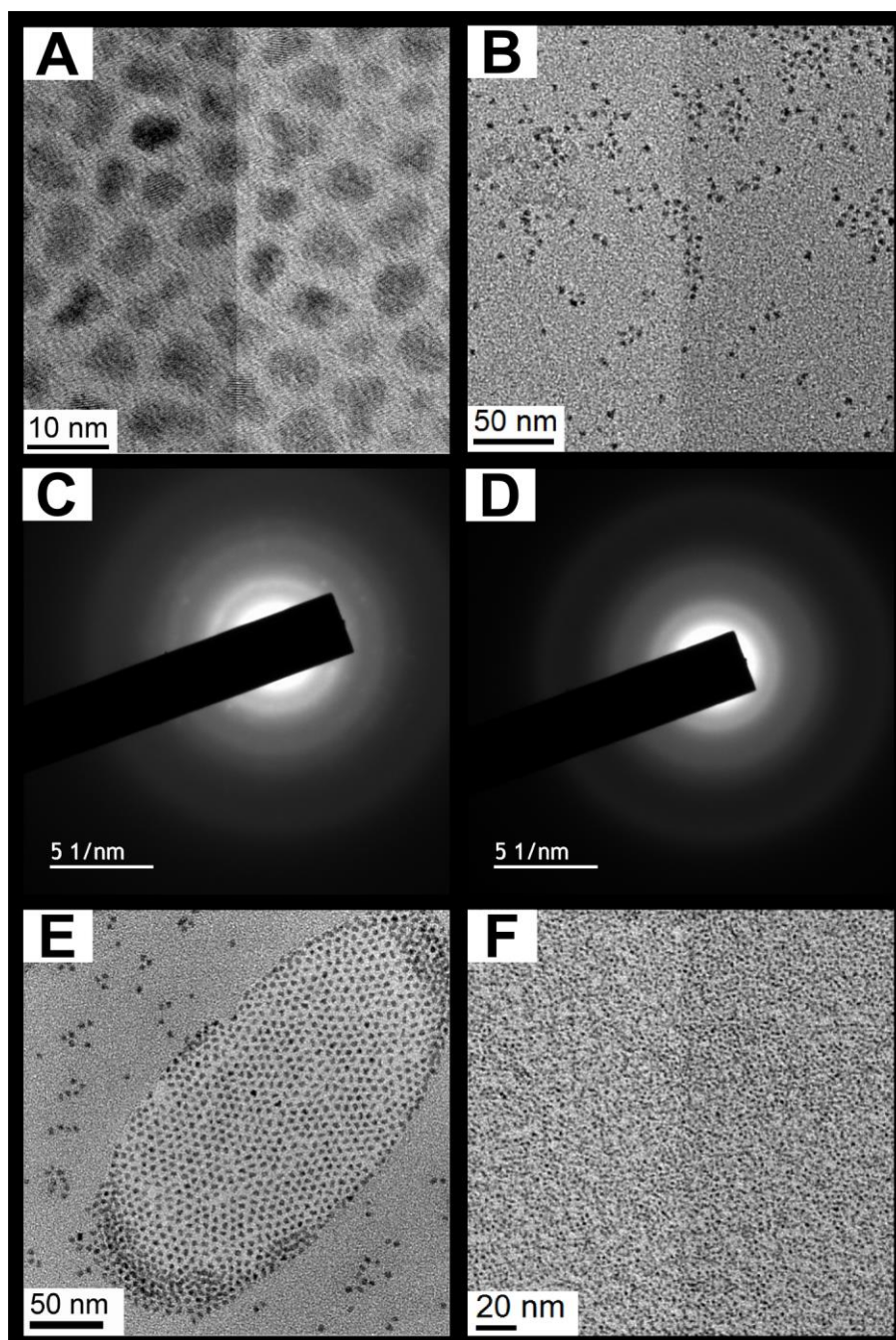


Figure 2. ((EDS spectra and HRTEM insets of: A: CdSe/ZnS QDs, B: CdSe/ZnS-CdS 3-1, C: CdSe/ZnS-HgS 3-1, D: CdSe-ZnS-CuS 3-1, E: InP/ZnS QDs and F: InP/ZnS-CdS.))

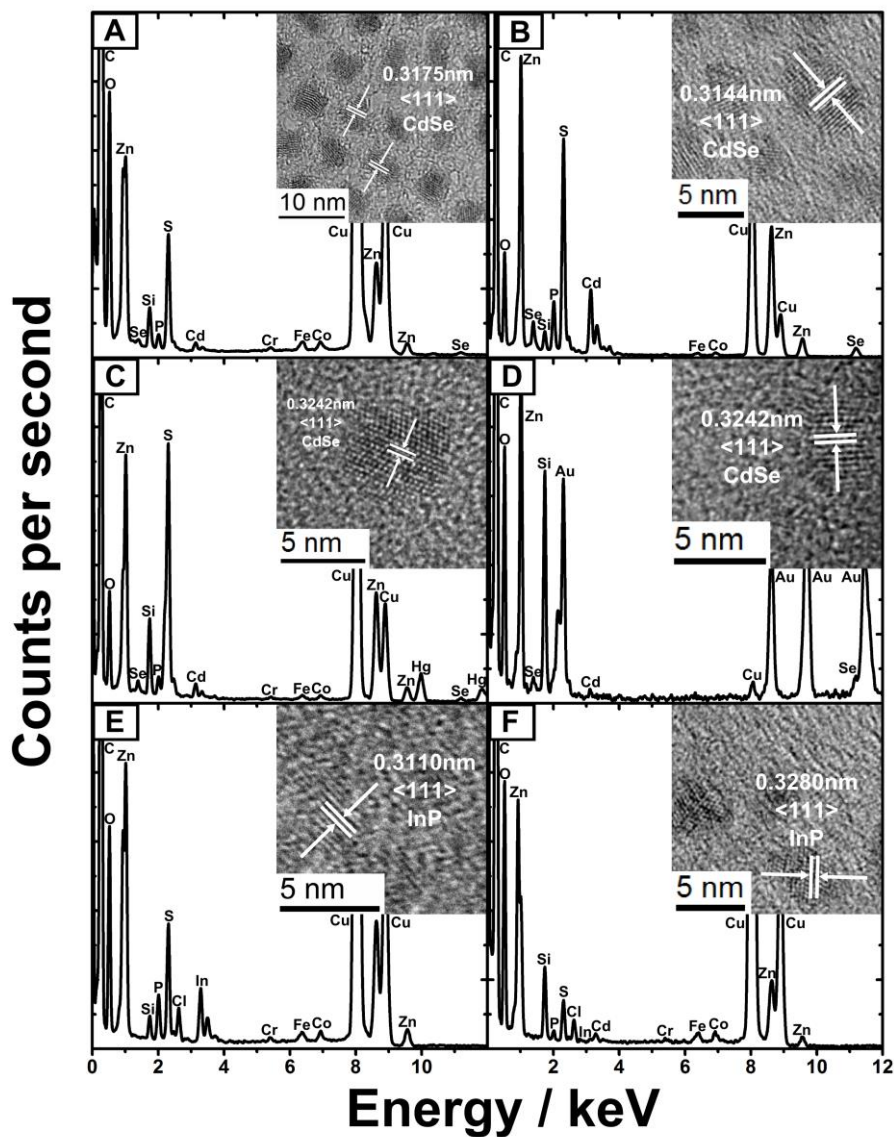
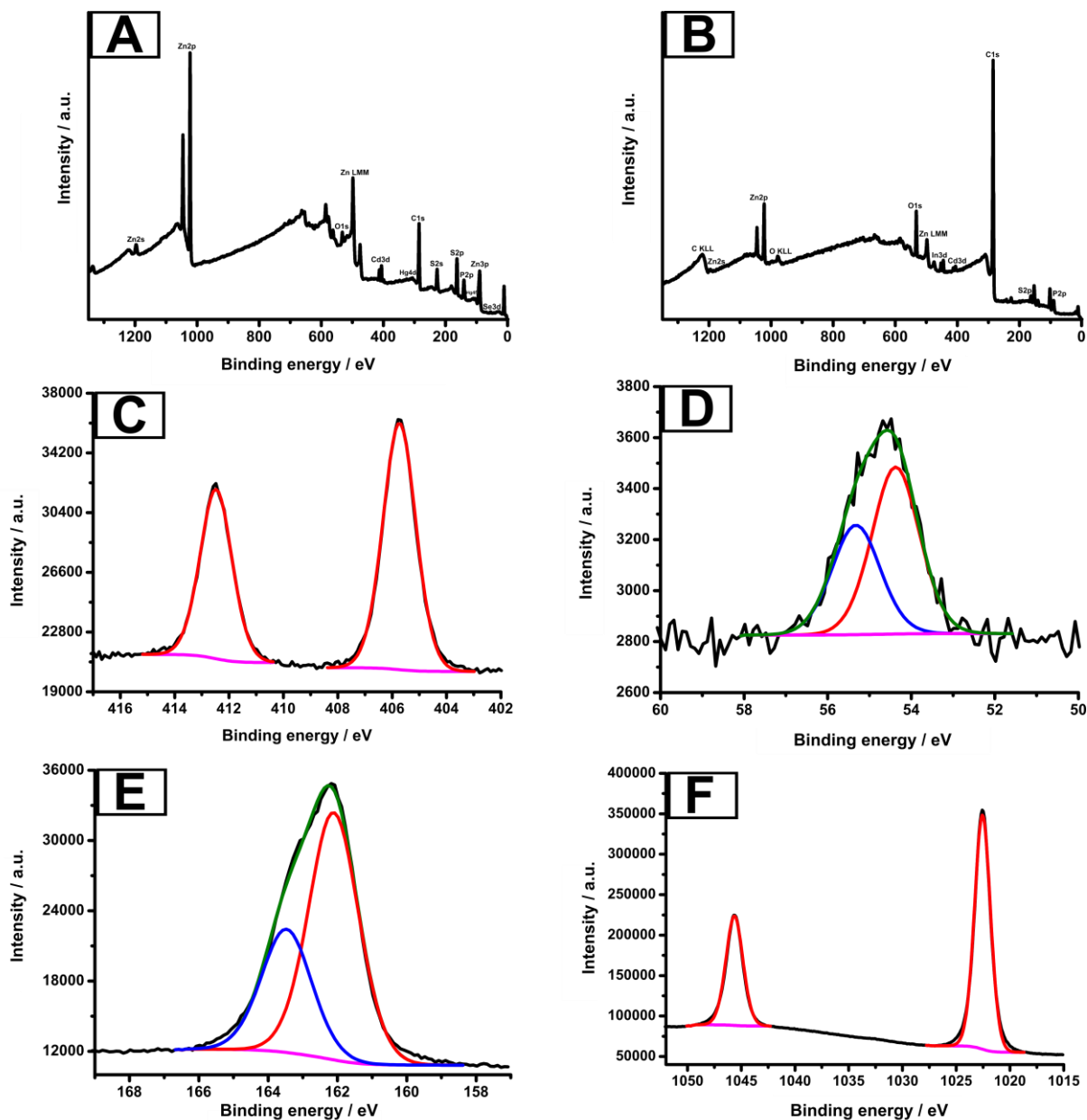


Figure 3. ((X-Ray Photoelectron Spectra of CdSe/ZnS-HgS 3-1. A: Survey, B: Survey of InP/ZnS-CdS 15-1, C: Fitted Cd3d scans, D: Fitted Se3d scans, E: Fitted S2p scans and F: Fitted Zn2p scans.))



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Figure 4. ((A: Photoluminescence spectra showing red shifting on addition of increasing amounts of Cd into the ZnS QD shell, B: The corresponding UV/vis spectra.))

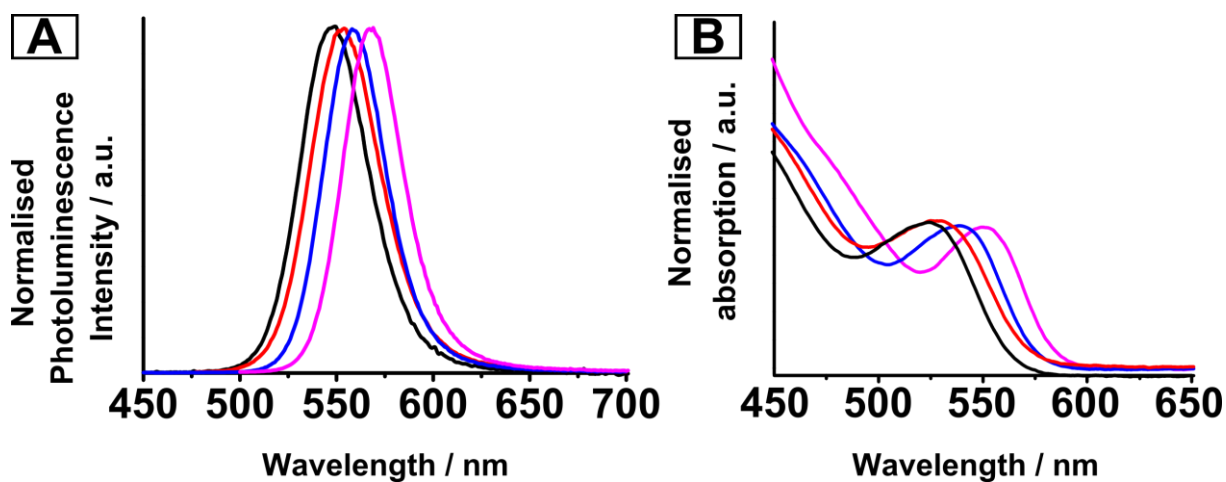


Figure 5. ((A: Photoluminescence spectra showing red shifting on addition of increasing amounts of Hg into the ZnS QD shell, B: The corresponding UV/vis spectra.))

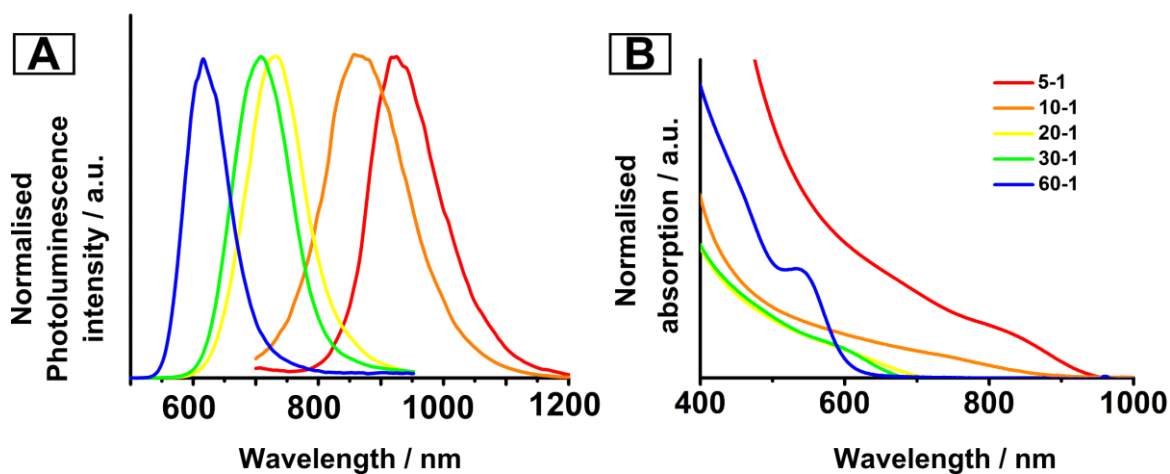
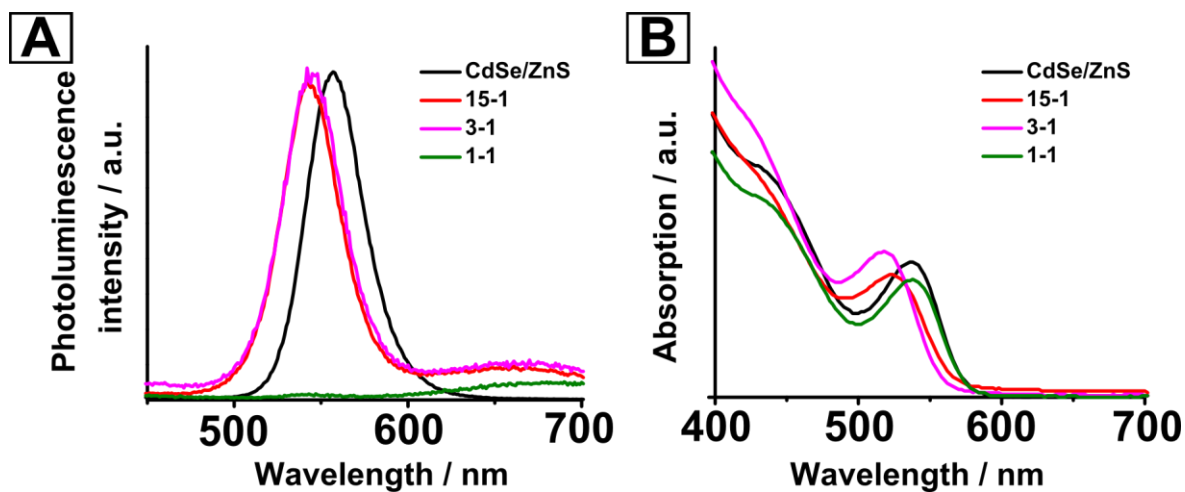


Figure 6. ((A: Normalised photoluminescence spectra showing the appearance of a second luminescence peak with increasing amounts of Cu in the ZnS QD shell, B: UV/vis spectra of the samples in A.))



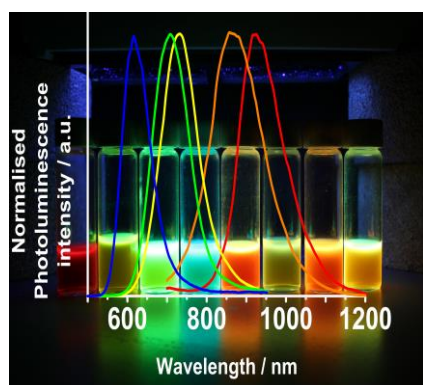
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The table of contents entry: Tri-light. Shell formation on core/shell II-VI and III-V semiconductor nanocrystals with the triad of Group IIB metals is presented, with luminescence and effect on quantum yield investigated. Shells are formed from the decomposition of as-synthesised metal dithiocarbamates; stable, single-source precursors for metal sulphides, making this a versatile and facile method for quantum dot shelling.

Keywords (core/shell; photoluminescence; quantum dots; single source)

Mr. Joseph C. Bear, Dr. Nathan Hollingsworth^{*}, Miss Anna R. Roffey, Dr. Paul D. McNaughton, Dr. Andrew G. Mayes, Mr. Mark S. Frost, Dr. Debra E. Whitehead, Mr. Thomas J. Macdonald, Prof. Thomas Nann, Dr. Wing H. Ng, Prof. Anthony J. Kenyon, Dr. Graeme Hogarth and Prof. Ivan P. Parkin^{*}

Doping Group IIB metal ions into quantum dot shells via the one-pot decomposition of metal-dithiocarbamates



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